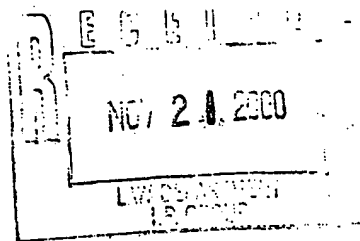


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A METHOD FOR PRODUCING ETHYLENE POLYMERS USING A  
SILICIC ACID-XEROGEL/CHROMIUM TRIOXIDE CATALYST

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The scope of the invention is a method for producing ethylene homopolymers and ethylene copolymers with  $\alpha$ -monoolefins using a silicic acid-xerogel/chromium trioxide catalyst, which is obtained by (1) first making a silicic acid-xerogel, by starting (1.1) with a silicic acid hydrogel that is spherical and is obtained by (1.1.1) introducing a water glass solution into a rotating mineral acid stream, (1.1.2) spraying the resulting silicic acid hydrogel in drops, (1.1.3) allowing the hydrosol in the spraying operation to solidify into a hydrogel, and (1.1.4) separating the hydrogel from salts, (1.2) extracting the water from the hydrogel by means of an alkanol or alkanone, (1.3) drying the dehydrated gel (xerogel formation), and (1.4) reducing the size of the xerogel, (2) then charging the xerogel with chromium trioxide or a chromium compound that converts to chromium trioxide, and (3) finally, heating the charged xerogel in a gas stream containing oxygen. The distinguishing characteristic is that an aluminoxane is used as cocatalyst in addition to the catalyst.

#### Claim

A method for producing ethylene homopolymers and ethylene copolymers with subordinate amounts of  $C_3$ - $C_{12}$  monoolefins incorporated by polymerization through the polymerization of the monomer or monomers at temperatures from 30-150°C and pressures from 2-150 bar using a silicic acid xerogel/chromium trioxide catalyst obtained by

(1) first making a finely divided silicic acid xerogel by

(1.1) starting with a silicic acid hydrogel that contains 10-25 wt% solids (calculated as silicon dioxide), which is largely spherical in shape, has a particle diameter in the range from 1-8 mm and is obtained by

(1.1.1) introducing a sodium or potassium water glass solution into a rotating stream of an aqueous mineral acid along or tangential to the stream,

(1.1.2) spraying the resulting silicic acid hydrosol into a gaseous medium in drops,

(1.1.3) allowing the sprayed hydrosol to solidify into a hydrogel in the gaseous medium, and

(1.1.4) separating the resulting largely spherical hydrogel from salts by washing without first aging it,

(1.2) extracting at least 60% of the water contained in the hydrogel from the hydrogel (1.1) by means of an organic liquid from the series of  $C_1$ - $C_4$  alkanols and/or  $C_3$ - $C_5$  alkanones,

(1.3) drying the resulting dehydrated gel that has been treated with the organic liquid until a loss of weight no longer occurs at 180°C under a vacuum of 10 torr over a period of 30 min (xerogel formation), and

(1.4) size reduction of the xerogel obtained in this way into particles with a diameter from 20-2000  $\mu$ m,

(2) then charging this xerogel (1) with the desired amount of chromium using a 0.05-5 wt% solution of chromium trioxide in a C<sub>3</sub>-C<sub>5</sub> alkanone or a 0.05-15 wt% solution of a chromium compound that converts to chromium trioxide under the conditions of step (3) in a C<sub>1</sub>-C<sub>4</sub> alkanol—where the relevant solvent must not contain more than 20 wt% water—while evaporating the solvent from the xerogel, and

(3) finally, holding the resulting product (2) in a water-free gas stream that contains oxygen in a concentration of over 10 vol% for 10-1000 min at a temperature from 400-1100°C,

characterized by the fact that, in addition to the catalyst, a cocatalyst is used which consists of an open chain or cyclic alumoxane of the formula



in which

R represents a C<sub>1</sub>-C<sub>12</sub> alkyl group,

m represents a number from 0-50, and

n represents a number from 2-20,

with the stipulation that the atomic ratio of chromium in the catalyst to aluminum in the cocatalyst is 1:1 to 1:300.

This invention lies within the scope of a method for producing ethylene homopolymers and ethylene copolymers with subordinate amounts of C<sub>3</sub>-C<sub>12</sub>, in particular C<sub>3</sub>-C<sub>8</sub>, α-monoolefins incorporated by polymerization, through the polymerization of the monomer or monomers at temperatures from 30-150, especially 60-120°C, and pressures from 2-150, especially 5-60 bar, using a silicic acid xerogel/chromium trioxide catalyst, which is obtained by

(1) first making a finely divided silicic acid xerogel by

(1.1) starting with a silicic acid hydrogel that contains 10-25, preferably 12-20 and especially 14-20 wt% solids (calculated as silicon dioxide), which are largely spherical in shape, have a particle diameter in the range from 1-8, especially 2-6 mm and are obtained by

(1.1.1) introducing a sodium or potassium water glass solution into a rotating stream of an aqueous mineral acid along or tangential to the stream,

(1.1.2) spraying the resulting silicic acid hydrosol into a gaseous medium in drops,

(1.1.3) allowing the sprayed hydrosol to solidify into a hydrogel in the gaseous medium,

and

(1.1.4) separating the resulting largely spherical hydrogel from salts by washing without first aging it,

(1.2) extracting at least 60%, especially at least 90%, of the water contained in the hydrogel from the hydrogel (1.1) by means of an organic liquid from the series of  $C_1$ - $C_4$  alkanols and/or  $C_3$ - $C_5$  alkanones,

(1.3) drying the resulting dehydrated gel which has been treated with the organic liquid until a loss of weight no longer occurs at  $180^\circ\text{C}$  under a vacuum of 10 torr over a period of 30 min (xerogel formation), and

(1.4) size reduction of the xerogel obtained in this way to particles with a diameter from 20-2000  $\mu\text{m}$ , especially 40-300  $\mu\text{m}$ ,

(2) then charging this xerogel (1) with the desired amount of chromium using a 0.05-5 wt% solution of chromium trioxide in a  $C_3$ - $C_5$  alkanone or a 0.05-15 wt% solution of a chromium compound that converts to chromium trioxide under the conditions of step (3) in a  $C_1$ - $C_4$  alkanol—where the relevant solvent must not contain more than 20, preferably no more than 5 wt% water—while evaporating the solvent from the xerogel, and

(3) finally holding the resulting product (2) in a water-free gas stream which contains oxygen in a concentration of over 10 vol% for 10-1000, especially 60-300 min at a temperature from 400-1100, especially  $700$ - $950^\circ\text{C}$ .

Polymerization methods of this kind are known, where in particular the method described in US Patent 4,037,042 can be considered as representative in this regard.

The said type of method, which has been successfully employed in industry, is like other methods with which parallels may be drawn, based on a chromium trioxide catalyst that is organized in a particular way.

The particular embodiments of the chromium trioxide catalysts are, as is known, designed in order to achieve certain goals such as, among others, the following:

(a) Catalysts that enable a high yield of polymerizate to be obtained, specifically catalysts with elevated productivity, i.e., ones in which the amount of polymer formed per unit of catalyst weight is elevated.

(b) Catalysts that enable polymers to be obtained which have no or only a relatively small decrease of the melt index ("MI drop") in further processing.

(c) Catalysts that develop their positive effects even at relatively low temperatures, which can be of importance, for example, for dry phase polymerizations.

(d) Catalysts through which the morphological properties of the polymers can be affected in certain ways, for instance in the sense of a uniform particle size and/or a high bulk weight, which can be of importance for industrial control of polymerization systems, processing of polymers and/or the processability of polymers.

(e) Catalysts that can be produced simply and safely and which are easily handled.

(f) Catalysts that enable the molecular weights of polymers to be controlled particularly effectively in polymerizations under the effect of molecular weight regulators such as hydrogen.

(g) Catalysts that allow polymers with particularly pronounced stress cracking resistance to be produced—a property that is particularly important, for example, for liquid containers, namely containers in which aggressive liquids are to be kept.

(h) Catalysts that are tailored to special polymerization processes, for instance those that are matched either to the specific peculiarities of suspension polymerization or to the specific peculiarities of dry phase polymerization.

(i) Catalysts by means of which polymers with, on the one hand, high molecular weight (finished product strength) and, on the other hand, problem-free processability can be obtained, i.e., high-molecular polymers that can be processed to flawless molded articles relatively rapidly at relatively low processing temperatures and/or relatively weak processing forces.

(j) Catalysts that lead to polymers with particularly high rigidity—a property that is desirable for many applications.

According to the practical knowledge up to now, there are among the many potential goals a number of goals that can be achieved through particular embodiments of the chromium trioxide catalysts only when other goals are cut back.

This gives the task that led to this invention: to develop further the proven method of the type defined at the start with the chromium trioxide catalyst of the type defined there so that the goals in accordance with (a), (b), (c), (g) and (i), taken together, can be achieved to a particularly high extent without a significant reduction of the goals in accordance with (d) and (j), again taken together.

It was found that this task can be solved if one conducts the method in question with the additional use of an alumoxane as a cocatalyst.

Accordingly, an object of the invention is a method for producing ethylene homopolymers and ethylene copolymers with subordinate amounts of  $C_3-C_{12}$ , especially  $C_3-C_8$   $\alpha$ -monoolefins incorporated by polymerization through the polymerization of the monomer or monomers at temperatures from 30-150, especially 60-120°C, and pressures from 2-150, especially 5-60 bar, by means of a silicic acid xerogel/chromium trioxide catalyst obtained by

(1) first making a finely divided silicic acid xerogel by

(1.1) starting with a silicic acid hydrogel that contains 10-25, preferably 12-20 and especially 14-20 wt% solid (calculated as silicon dioxide), which is largely spherical in shape, has a particle diameter in the range from 1-8, especially 2-6 mm and is obtained by

(1.1.1) introducing a sodium or potassium water glass solution into a rotating stream of an aqueous mineral acid along or tangential to the stream,

(1.1.2) spraying the resulting silicic acid hydrosol into a gaseous medium in drops,

(1.1.3) allowing the sprayed hydrosol to solidify into a hydrogel in the gaseous medium and

(1.1.4) separating the resulting largely spherical hydrogel from salts by washing without first aging it,

(1.2) extracting at least 60%, especially at least 90% of the water contained in the hydrogel from the hydrogel (1.1) by means of an organic liquid from the series of  $C_1$ - $C_4$  alkanols and/or  $C_3$ '- $C_5$  alkanones,

(1.3) drying the resulting dehydrated gel that has been treated with the organic liquid until a loss of weight no longer occurs at  $180^\circ\text{C}$  under a vacuum of 10 torr over a period of 30 min (xerogel formation) and

(1.4) size reduction of the xerogel obtained in this way to particles with a diameter from 20-2000  $\mu\text{m}$ , especially 40-300  $\mu\text{m}$ ,

(2) then charging this xerogel (1) with the desired amount of chromium using a 0.05-5 wt% solution of chromium trioxide in a  $C_3$ - $C_5$  alkanone or a 0.05-15 wt% solution of a chromium compound that converts to chromium trioxide under the conditions of step (3) in a  $C_1$ - $C_4$  alkanol—where the relevant solvent must not contain more than 20, preferably no more than 5 wt% water—while evaporating the solvent from the xerogel, and

(3) finally holding the resulting product (2) in a water-free gas stream that contains oxygen in a concentration of over 10 vol% for 10-1000, especially 60-300 min at a temperature from 400-1100, especially  $700$ - $950^\circ\text{C}$ .

The method in accordance with the invention is characterized by the fact that, in addition to the catalyst, a cocatalyst is used which consists of a—preferably—open-chain or—also—cyclic alumoxane of the formula



in which

R represents a  $C_1$ - $C_{12}$  alkyl group, especially  $C_1$ - $C_6$  alkyl group, most especially the isobutyl group,

m represents a number from 0-50, preferably 0-20, and especially 0-10, and

n represents a number from 2-20, especially 3-10,

with the stipulation that the atomic ratio of chromium in the catalyst to aluminum in the cocatalyst is 1:1 to 1:300, preferably 1:1 to 1:100 and especially 1:1 to 1:50.

The following details may be given regarding the preparation of the catalysts to be used in the method in accordance with the invention:

(1) First step

(1.1) Characteristic for this step is the use of a silicic acid hydrogel that has a relatively high solids content, is largely spherical and, especially, has been prepared in a particular way. This particular way of production is described in detail in substeps (1.1.1), (1.1.2) and (1.1.3), for example in U.S. Patent No. 3,872,217; a description of the same substeps and, in addition, substep (1.1.4) will be found, for example, in US Patent No. 4,037,042. The material disclosed so far in said two patents, via the citation, should be a part of this description, so that in this description, relevant, more detailed presentations are not necessary.

(1.2) The extraction of the water from the silicic acid hydrogel by means of the organic liquid indicated above can take place in conventional extraction devices. Suitable devices are, for example, column extractors. The following (arranged by decreasing effectiveness, but not by decreasing economic efficiency) have proven themselves as organic liquids from among the ethanols: tert-butanol, isopropanol, ethanol and methanol. Of the alkanones, which overall are to be preferred over alkanols, acetone has proven itself above all. It goes without saying that the organic liquid can consist of one or several of the individual components in question, where in each case, the liquid should contain less than 5 and preferably less than 3 wt% water before the extraction.

(1.3) The conversion of the gel treated with the organic liquid to the xerogel (drying) can again take place in the appropriately conventional drying devices. Here, one obtains the best results when drying is carried out at product temperatures from 80-200°C and pressures from 1-250 torr, where, due to the vapor pressure, one should assign an increasing pressure to an increasing temperature and vice versa. The drying process, especially at relatively high pressures, can be accelerated through flowing carrier gases, for instance, nitrogen.

(1.4) Obtaining xerogel particles with a specific diameter is not substantially difficult. It can take place in a simple way, for example, the product obtained from step (1.3) can be ground and fractionated through screens.

(2) Second step

When charging the xerogel with the chromium component, one can expediently proceed so that the xerogel is suspended in a solution of chromium trioxide or a chromium compound that converts to chromium trioxide under the conditions of step (3) (where the amounts are chosen so that the desired xerogel:chromium ratio results) and with permanent, as homogeneous as possible mixing of the batch, evaporating its liquid components out—thus, alkanone or alkanol and possibly water. Here it is most expedient to operate at temperatures from 20-150°C and pressures from 10-760 torr. It is not critical if the xerogel charged with the chromium component still contains a certain residual amount of moisture (volatile components no more than 20, especially no more than 10 wt%, with respect to the xerogel). Chromium components



that are suitable in this regard are, above all, chromium trioxide and chromium hydroxide, as well as soluble salts of trivalent chromium with an organic or inorganic acid like acetate, oxalate, sulfate, nitrate; particularly suitable are the salts of those acids that convert residue-free to chromium oxide upon activation. Chromium compounds in the form of chelates, such as chromium acetylacetonate, can also be used.

### (3) Third step

This step serves to activate the catalysts; it can be carried out in a relatively conventional way: one known from literature and practice, i.e., in particular, in conditions that guarantee that in the prepared catalyst, the chromium, at least partially, is not in a state other than hexavalent.

A characteristic feature of the method in accordance with the invention is that the chromium trioxide catalyst that is described above and which is substantially known is used with the additional concomitant use of an alumoxane of the formulas defined in more detail above, as cocatalysts.

Specific examples of suitable cocatalysts of the indicated kind are: tetraisobutyldialumoxane, pentaisobutyltrialumoxane and hexaisobutyltetraalumoxane as open-chain representatives, and triisobutyltrialumoxane, tetraisobutyltetraalumoxane and pentaisobutylpentaalumoxane as cyclic representatives.

Finally, the following may be mentioned in regard to the method in accordance with the invention as a whole:

The polymerization method as such can, while observing the characterizing feature, be carried out in practically all relevant conventional industrial equipment, for instance, as a batch, cyclic or continuous process, be it a suspension polymerization process, solution polymerization process or dry phase polymerization process; where, however, the greatest advantages are offered in the first of these. The selected industrial arrangements—in other words the industrial variations of polymerization of olefins following Phillips—are well known from the literature and practice, so that here, more detailed comments are unnecessary. However, it still should be noted that the catalysts can be brought together with the cocatalysts outside of the polymerization vessel or in it; in the latter case, for instance, through spatially separate feeding of the components, which can be handled in the form of a suspension (catalyst) or solution (cocatalyst).

In addition, it still should be noted that the new method mainly lends itself to the production of homopolymers of ethylene. In the production of copolymers of ethylene with  $\alpha$ -monoolefins, propene, 1-butene, 1-hexene and 1-octene particularly are possibilities as  $\alpha$ -monoolefins. The co-use of molecular weight regulators such as, in particular, hydrogen, is possible with good success in the method in accordance with the invention.

### Example

#### Preparation of the silicic acid xerogel

The mixing nozzle shown in one of the figures of U.S. Patent No. 3,872,217 which had the following characteristics was used: the diameter of the cylindrical mixing chambers formed from a plastic tube was 14 mm, the mixing chamber length (including the postmixing section) was 350 mm. Near the closed-end inlet side of the mixing chamber was a tangential inlet drilling 4 mm in diameter for the mineral acid. There were four additional drillings, also 4 mm in diameter, with the same inlet direction for the water glass solution, with the distance between the drillings measured in the long direction of the mixing chamber being 30 mm. Accordingly, the ratio of length to diameter of the primary mixing zone was approximately 10. This ratio was 15 for the subsequently connected secondary mixing zone. A flattened, slightly kidney shaped tube piece was pushed over the outlet end of the plastic tube as the extrusion die.

This mixing device was charged with 325 L/h 33 wt% sulfuric acid at 20°C at an operating pressure of about 3 bar, and with 1100 L/h water glass solution (prepared from technical grade water glass containing 27 wt% SiO<sub>2</sub> and 8 wt% Na<sub>2</sub>O by dilution with water) with a weight per liter of 1.20 kg/L and a temperature of likewise 20°C at a pressure of about 3 bar. In the mixing chamber lined with the plastic tube, an unstable hydrosol with a pH between 7 and 8 was formed by progressive neutralization, and it remained in the postmixing zone for approximately another 0.1 sec for complete homogenization before it was sprayed into the atmosphere through the nozzle as a flat liquid jet. During its flight through the air, the jet broke up into individual droplets, which as a consequence of surface tension changed to a largely spherical shape and which solidified to hydrogel spheres while still in flight over a period of about 1 sec. The spheres had a smooth surface, were transparent, contained about 17 wt% SiO<sub>2</sub> and had the following particle size distribution:

>8 mm	10 wt%
6-8 mm	45 wt%
4-6 mm	34 wt%
<4 mm	11 wt%

The hydrogel spheres were collected at the end of their flight in a wash tower, which was nearly completely filled with hydrogel spheres and in which the spheres were immediately, without aging, washed with a weak ammoniacal water solution heated to about 50°C in a continuous counterflow process until they were salt free.

The spheres, which had a diameter in the range from 2-6 mm, were isolated by screening, and 112 kg of these spheres were put into an extraction vessel with inflow at the top, a sieve bottom and a gooseneck overflow, which attached at the bottom of the vessel and kept the liquid level in the drum at a height so that the hydrogel spheres were completely covered with liquid.

Then ethanol was supplied at a rate of 60 L/h until the density of the ethanol-water mixture exiting at the overflow had fallen to  $0.826 \text{ g/cm}^3$ ; it was then that about 95% of the water contained in the hydrogel had been extracted.

The resulting spheres were dried for 8 h at  $180^\circ\text{C}$  under a vacuum of 10 torr; at this point no weight loss occurred under these conditions over a period of 30 min.

Then the dried spheres were ground and the xerogel particles that had a diameter from 100-200  $\mu\text{m}$  were separated by screening.

#### Preparation of the catalyst

15 kg of the above-described xerogel and 40 L of an approximately 1 wt% solution of chromium trioxide in acetone was put into a double-cone mixer. The acetone was distilled out in a water jet vacuum by rotating the mixer, which was externally heated with steam to  $110^\circ\text{C}$ .

The resulting product was heated for 4 h to a temperature of  $870^\circ\text{C}$  in a fluidized bed that was fluidized with air and then again cooled. Starting with  $140^\circ\text{C}$ , nitrogen was passed through the fluidized bed in order to remove traces of oxygen (which are troublesome in polymerization).

The resulting catalysts had an analytically determined chromium content of about 0.0002 mol/g.

#### Polymerization

The process was carried out in a 10-L pressurized autoclave. It was heated to  $105^\circ\text{C}$  and flushed several times with ethylene. Then, 5 L isobutane, to which 0.79 mL of a 20 wt% solution of tetraisobutyldialuminoxane in n-heptane had been added, was supplied with stirring. After the desired reaction temperature of  $105^\circ\text{C}$  was reached, 250 mg of the above-described catalyst was supplied by means of nitrogen, so that the pressure in the autoclave before the feed of ethylene was 25 bar. The selected atomic ratio of chromium in the catalyst to aluminum in the cocatalyst corresponded to 1:15.

Then, ethylene was pressurized stepwise up to a total pressure of 41 bar, and at a constant reaction temperature, repressurized in the pressure interval from 39-41 bar in correspondence with the progress of the polymerization. The polymerization was interrupted by depressurization after a reaction time of 112 min.

1920 g grainy polyethylene were obtained, which corresponds to a productivity of 7680 g polyethylene per g of catalyst.

The polyethylene had the following characteristics:

Melt-flow index (MFI 190°C/10.0 kp, according to DIN 53 735)	=	2.0 g/10 min
(Upon granulation of the material under appropriate conventional conditions with a granulator extruder at a maximum compound temperature of 210°C, this value fell by 4%)		
Bulk weight (according to DIN 53 468)	=	280 g/L
Stress cracking resistance (ESCR (h), according to ASTM D-1693-70)	=	35 h
Intrinsic viscosity (according to DIN 53 728)	=	3.0 dL/g
HL melt-flow index (HLMFI 190°C/21.6 kp, according to DIN 53 735)	=	13.6 g/10 min
Shear modulus G (according to DIN 53 445)	=	900 N/mm <sup>2</sup> .

#### Comparison test

This test was carried out identically to the example (even with regard to the measurement of the characteristic data) with the sole exception that no cocatalyst was used.

500 g polyethylene were obtained in this way.

The characteristic data were as follows:

Melt-flow index	=	6.14 g/10 min
(Upon granulation, this value fell by 22%)		
Bulk weight	=	290 g/L
Stress cracking resistance	=	20 h
Intrinsic viscosity	=	2.3 dL/g
HL melt-flow index	=	34.5 g/10 min
Shear modulus G	=	910 N/mm <sup>2</sup> .